

ERDC/EL TR-01-6

Environmental Laboratory



**US Army Corps
of Engineers®**
Engineer Research and
Development Center

Cost and Performance Report for Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) Thermal Desorption Sampler for Volatile Organic Compounds

Karen F. Myers, Jed Costanza, Dan Y. Eng,
Richard A. Karn, Karl F. Konecny, and William M. Davis

February 2001

20010417 044

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products.

The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.



PRINTED ON RECYCLED PAPER

Cost and Performance Report for Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) Thermal Desorption Sampler for Volatile Organic Compounds

by Karen F. Myers, Jed Costanza, Dan Y. Eng, Richard A. Karn,
Karl F. Konecny, William M. Davis

Final report

Approved for public release; distribution is unlimited

Prepared for Environmental Security Technology Certification Program
U.S. Army Engineer Research and Development Center
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Contents

Preface	vi
Abbreviations and Acronyms.....	vii
1—Introduction.....	1
2—Technology Description	2
Thermal Desorption Sampler System	2
Thermal desorption sampler probe	3
Ion trap mass spectrometer analytical system	4
Site Characterization Penetrometer and Analysis System (SCAPS).....	5
Personnel Training Requirements.....	7
Advantages of the Technology	7
Limits of the Technology.....	7
Truck-mounted cone penetrometer access limits.....	7
Cone penetrometer advancement limits.....	8
TDS limitations	8
ITMS limitations	8
Extremely high level contamination carryover	9
3—Demonstration Design.....	11
Performance Objectives.....	11
Physical Setup and Operation.....	11
Monitoring Procedures	12
Demonstration Site Facility Background and Characteristics.....	13
Cold Regions Research and Engineering Laboratory	13
CRREL history.....	13
CRREL characteristics	14
Lake City Army Ammunition Plant site	15
LCAAP history.....	15
LCAAP characteristics	15
Longhorn Army Ammunition Plant site	16
LHAAP history	17
LHAAP characteristics.....	17

4—Performance Assessment.....	20
Comparison of TDS Sampler Technology with Conventional Technology...	20
Cold Regions Research and Engineering Laboratory.....	21
Lake City Army Ammunition Plant.....	23
Longhorn Army Ammunition Plant.....	23
Sample Matrix Effects on the TDS System	24
Contaminant Carryover	25
Quality Assurance Assessment.....	25
TDS system	26
EPA Method 8260B.....	27
TDS Method Detection Limits	27
5—Cost Assessment	29
TDS Sampler Cost Performance.....	29
Cost Comparison of the TDS System to Conventional and Other Technologies	30
6—Implementation Issues.....	32
Regulatory Issues.....	32
Lessons Learned	33
References.....	34
Appendix A: Points of Contact	A1
SF298	

List of Figures

Figure 1. Thermal desorption sampler system	3
Figure 2. Thermal desorption sampler probe	4
Figure 3. TDS probe sampler collection	5
Figure 4. Army SCAPS truck	6
Figure 5. Ex situ TDS mode	12
Figure 6. Cold Regions Research and Engineering Laboratory, Hanover, NH	14
Figure 7. Lake City Army Ammunition Plant, Independence, MO	16

Figure 8.	Longhorn Army Ammunition Plant, Marshall, TX	19
Figure 9.	CRREL data comparison	22
Figure 10.	Changes in TCE contamination at CRREL relative to soil type	22
Figure 11.	LCAAP data comparison.....	23
Figure 12.	LHAPP data comparison	24
Figure 13.	TDS system recovery after analysis of a highly contaminated sample.....	26

List of Tables

Table 1.	TDS System Demonstration Locations.....	12
Table 2.	Summary of Field Sampling at TDS Demonstrations Sites	20
Table 3.	Desorption Efficiencies by Matrix and Contaminant.....	24
Table 4.	Comparison of Unit Costs for the TDS Sampler and Conventional Technologies	30

Preface

Several organizations and individuals cooperated to make this demonstration possible. Dr. Jeff Marqusee, Director of the Department of Defense Environmental Security Technology Certification Program (ESTCP) sponsored the technology verification demonstrations and independent evaluations for the technology certification. Dr. M. John Cullinane, U.S. Army Engineer Research and Development Center (ERDC), was the program manager and Mr. George Robataille was the technical monitor for the U.S. Army Environmental Center.

Personnel who cooperated in the execution of the study and the preparation of this report included Ms. Karen F. Myers and Mr. Richard A. Karn, Environmental Chemistry Branch (ECB), Environmental Engineering Division (EED), Environmental Laboratory (EL), ERDC; Mr. Karl F. Konecny, Environmental Restoration Branch (ERD), EL, ERDC; Mr. Dan Y. Eng, Design and Development Branch (JD), Instrumentation Systems Development Division (ISDD), Information Technology Laboratory (ITL), ERDC; Dr. William M. Davis, Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), EL, ERDC; and Mr. Jed Costanza, Naval Facilities Engineering Service Center. The authors wish to acknowledge Ms. Beverly Adkison, Mississippi Department of Environmental Quality; Mr. Richard H. Burrow and Mr. Jeff F. Powell, ITL; and Mr. Don Harris, DPW, for technical support. Mr. John H. Ballard, EL, and Mr. Jeff F. Powell, ITL, reviewed the report.

This report was prepared under the general supervision of Ms. Ann B. Strong, Chief, ECB; Mr. Norman Francingues, Jr., Acting Chief, EED; Dr. Richard E. Price, Chief EPED; Dr. John Keeley, Acting Director, EL; Mr. Dan Y. Eng, Acting Chief, JD; Dr. Charles Robert Welch, Chief, ISDD; and Mr. Timothy D. Ables, Acting Director ITL.

At the time of publication of this report, Dr. James R. Houston was Director of ERDC, and COL James S. Weller, EN, was Commander.

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products.

Abbreviations and Acronyms

µg/g	Microgram per gram
AFB	Air Force Base
AOC	Areas of Concern
ASTM	American Society for Testing and Materials
BETX	Benzene, ethylbenzene, toluene, xylene
BGS	Below ground surface
BRSA	Bush River Study Area, U.S. Army Aberdeen Proving Ground
°C	Degree(s) Celsius
Cal EPA-DTSC	California Environmental Protection Agency, Department of Toxic Substance Control
cm	Centimeter
CPT	Cone penetrometer test
CRREL	U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory
DCE	Dichloroethene
DGCS	Davis Global Communications Site, McClellan Air Force Base
DoD	Department of Defense
DSITMS	Direct sampling ion trap mass spectrometer
ECB	Environmental Chemistry Branch
EI	Electron impact ionization
EPA	U.S. Environmental Protection Agency
ERDC	U.S. Army Engineer Research and Development Center
GC/MS	Gas chromatograph/mass spectrometer
ha	Hectare
ITMS	Ion trap mass spectrometer

km	Kilometer
kl	Kiloliter
LAP	Load and pack
LCAAP	Lake City Army Ammunition Plant
LHAAP	Longhorn Army Ammunition Plant
LIF	Laser induced fluorescence
MDL	Method detection limit
mg/kg	Milligrams per kilogram
mg/L	Milligrams per liter
ml	Milliliter
ml/min	Milliliters per minute
mm	Millimeter
MT	Metric ton
m/z	Mass to charge ratio of an ion
ng/g	Nanagram per gram
OSHW	U.S. EPA Office of Solid and Hazardous Waste
PCE	Tetrachloroethene
PE	Performance evaluation
PEP	Propellant, explosive, and pyrotechnics
ppb	Parts per billion; equivalent to ng/g, µg/kg and µg/L
P&T	Purge and trap sample concentrator
PV	ex situ TDS prove verification sample by ITMS
QC	Quality control
r ²	Correlation coefficient
SCAPS	Site Characterization and Analysis Penetrometer System
SWMU	Solid waste management units
TCE	Trichloroethene
TDS	Thermal desorption VOC sampler
U.S.	United States
USACE	United States Army Corps of Engineers
VOC	Volatile organic compound
WES	Waterways Experimental Station

1 Introduction

The Thermal Desorption Sampler (TDS) is designed to collect a soil sample and perform an in situ analysis for the presence of Volatile Organic Compounds (VOCs). The TDS system performs rapid field screening to determine either the presence or absence of VOCs within the unsaturated subsurface soil of a site. In addition, the TDS interfaced to an Ion Trap Mass Spectrometer (ITMS) provides identification of specific analytes based on their mass spectra and provides estimates of contaminant concentrations. The TDS system is deployed by the Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS).

The TDS principle of operation is based on capturing a known volume of subsurface soil in situ, heating the sample chamber, and purging the VOC contaminants with helium carrier gas while heating the soil. The VOCs in the carrier gas are then collected on a sorbent trap that concentrates the VOCs prior to introduction into the ITMS for quantification and identification of the VOCs.

The TDS system was demonstrated at five separate DoD facilities located in diverse geological conditions. The TDS/ITMS system performed well during the collection and analysis of 170 in situ samples. More than 600 verification samples were also collected for off-site laboratory analysis. There was a strong correlation between the off-site laboratory verification sample results and the TDS ex situ mode analysis results.

Limitations of the TDS system involve the mechanical operation of the probe and the desorption efficiency of the sampler. Lithologies containing gravels, cobbles, and clay may prevent the sample chamber from opening properly and filling with soil. Clay and saturated soils may exhibit reduced VOC desorption efficiencies that necessitate heating the sample chamber for increased sampling times.

Cost of operating the TDS system is comparable to conventional sample collection and analysis techniques. The main savings produced by using the TDS system are a reduction in time spent characterizing a site, the reduced exposure of workers to contaminants, and the minimization of investigation wastes.

2 Technology Description

The TDS was designed to collect a soil sample and perform an in situ analysis for the presence of Volatile Organic Compounds (VOCs). The TDS system performs rapid field screening to determine either the presence or absence of VOCs within the subsurface unsaturated soil of a site. In addition, the TDS provides identification of specific analytes based on their mass spectra and provides estimates of contaminant concentrations. The TDS system is deployed by the Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS).

Thermal Desorption Sampler System

The TDS principle of operation is based on capturing a known volume of subsurface soil in a sample chamber in situ and purging the VOC contaminants with helium carrier gas while heating the sample chamber. The TDS system (shown in Figure 1) is comprised of a sample collection probe linked indirectly by an umbilical to an Ion Trap Mass Spectrometer (ITMS). The 61-m (200-ft) umbilical cable consists of heat shrink plastic that contains:

- a.* An unheated, 1.6-mm- (1/16-in.-) diameter, fused silica-lined stainless steel analyte transfer line.
- b.* Three 3.1-mm- (1/8-in.-) diameter lines supplying carrier gas to support mechanical functions.
- c.* The heater, thermocouple, and position indicator wires.

Soil gases desorbed from the sample chamber within the TDS probe are returned to the surface via the analyte transfer line where they are collected on a sorbent trap. Samples are collected under vacuum, as needed, to keep a balance between the flow up through the analyte transfer line and the flow down through the carrier gas line. The sorbent trap can be extracted with methanol or heated at a controlled rate to force analytes present to enter the ITMS for analysis.

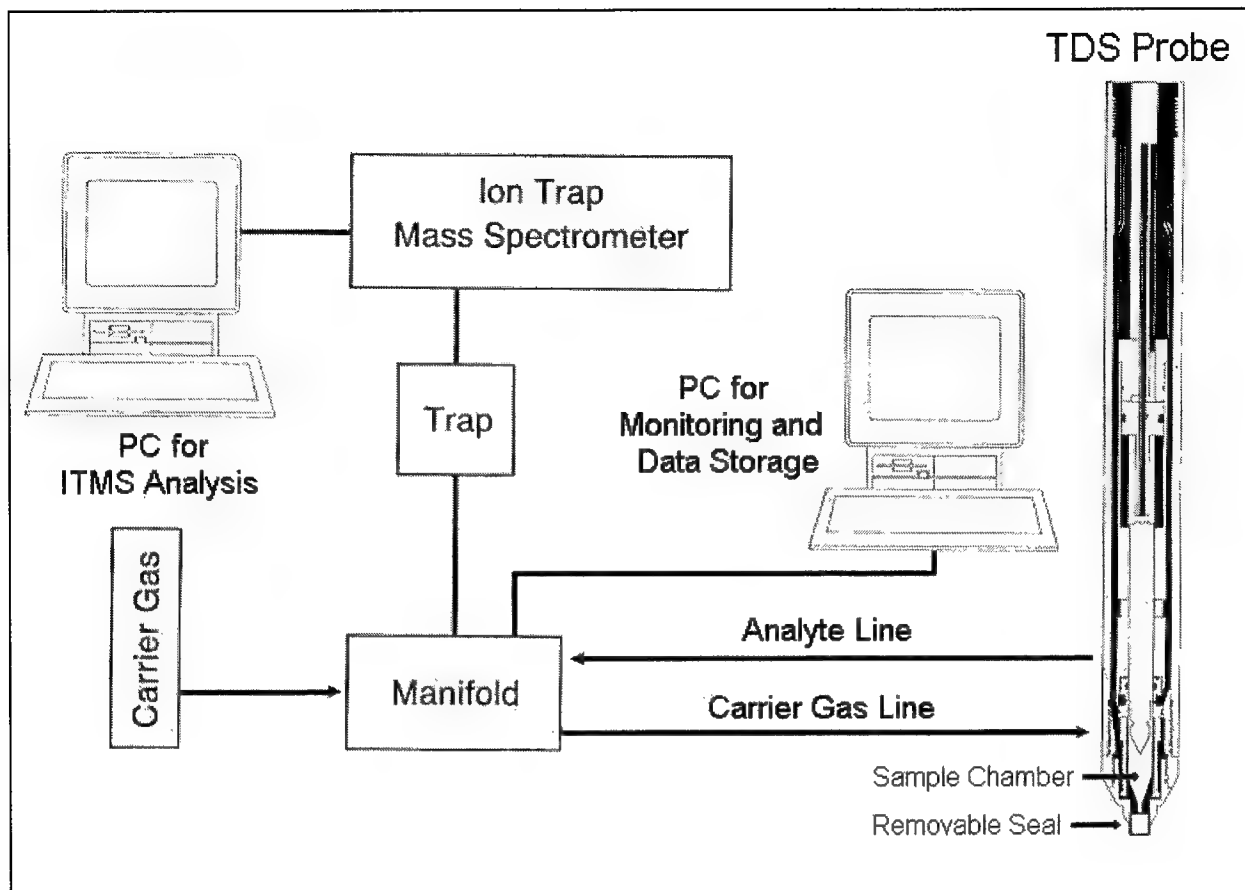


Figure 1. Thermal desorption sampler system

Thermal desorption sampler probe

The TDS probe design is a series of steel cylinders with gas channels and piston chambers made tight by o-rings (Figure 2).

Figure 3 shows the operation of the TDS probe during sample collection. A central actuator rod with retractable tip is held in place by locking lugs in the closed position while the probe is being pushed into the ground. Once the probe reaches sampling depth, the locking lugs are pneumatically released and the piston is retracted to reveal the sample chamber. At sampling depth, the probe is pushed an additional 4.5 to 5.1 cm (1.75 to 2.0 in.) to acquire a sample of soil of a known diameter and an estimated volume. Depending upon soil density, the plug weight ranges from 3.5 to 5.0 grams. Helium is introduced through a stainless steel tube located along the inner wall of the outer housing at a rate of 50 ml/min. The gas enters the sample chamber area from behind and below. It is preheated to temperatures between 170 and 200 °C as it moves across the surface of the heater before sweeping upward over the soil sample to purge the VOCs as they are volatilized into the chamber. The gas carries the volatilized analytes up through the analyte line and into a sample collection device at the surface (Figure 1). Once the analytes have been desorbed from the soil, the soil is

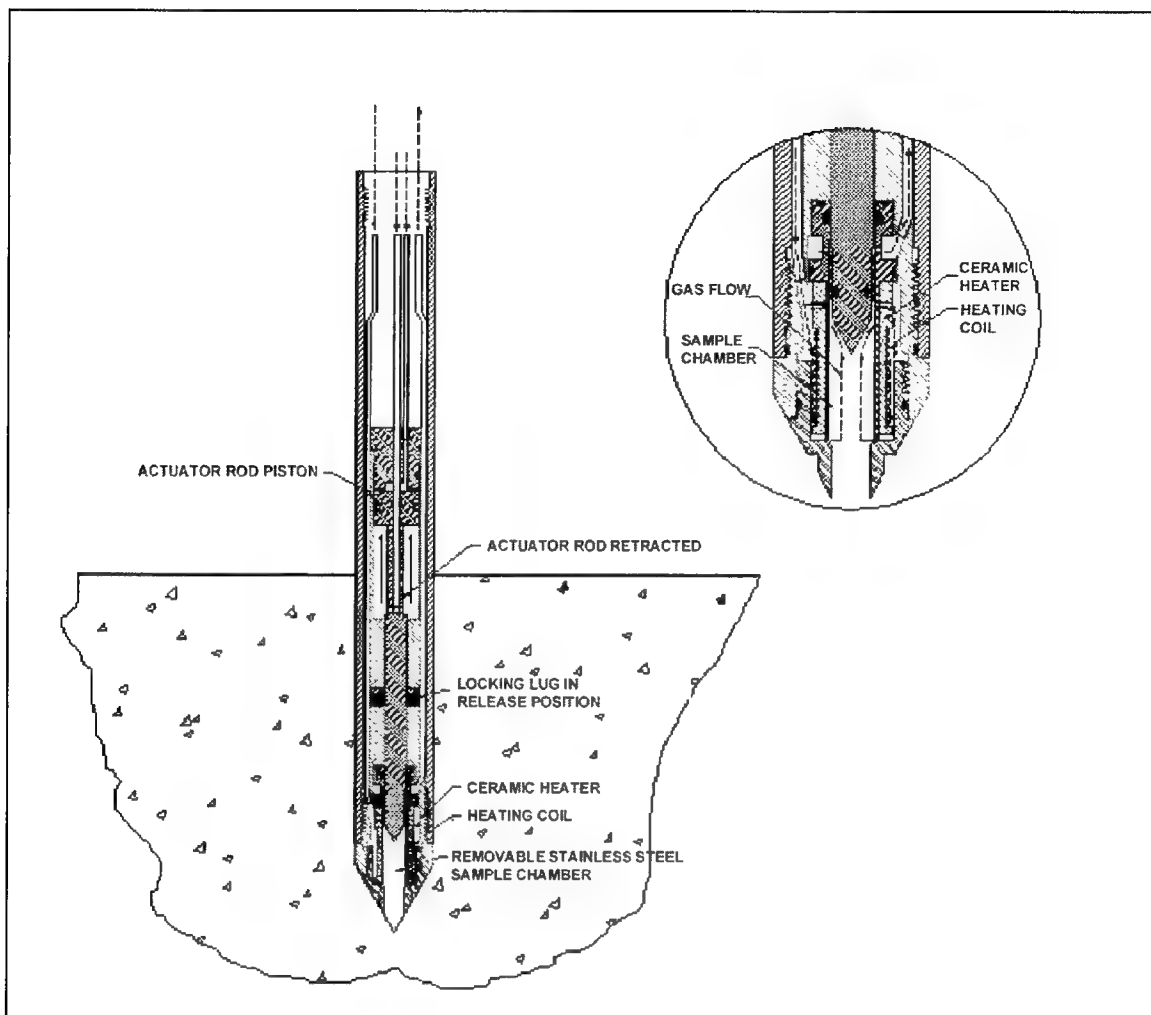


Figure 2. Thermal desorption sampler probe

ejected by forcing a burst of high-pressure gas down the line while lowering the actuator rod. A sensor in the probe indicates the rod's position to the operator at the surface. After the spent soil is ejected and the actuator rod is locked in the closed position, the TDS probe is pushed to a new depth and the sampling process is repeated.

Ion trap mass spectrometer analytical system

The ITMS analytical system is a field portable ITMS with an OI Analytical purge and trap (P&T) sample concentrator as the analyte introduction device. Volatilized analytes are collected on the sorbent trap attached to the control manifold. To capture the broadest range of VOCs, an OI Analytical style No. 9 trap filled with a mixture of Tenax, silica gel, and charcoal is used. Once the TDS probe collects a sample, it can be analyzed in one of two ways. If low level concentrations are expected (less than 50 ppb of analyte per 5 gram mass of soil), the trap can be inserted into the P&T and desorbed directly in to the ITMS. If

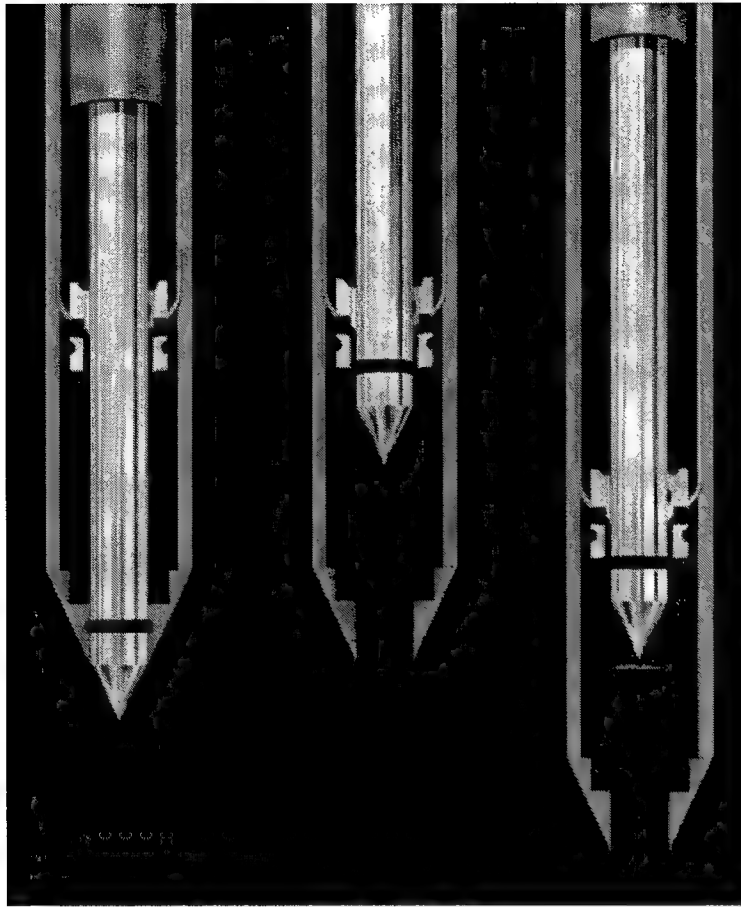


Figure 3. TDS probe sampler collection

higher concentrations are suspected, the trap is eluted with 1 ml of P&T grade methanol. An aliquot of the methanol is placed into water in the P&T vessel then desorbed into the ITMS for analysis and quantitation. After the VOCs are eluted from the trap, any remaining methanol is flushed with inert gas. The trap is placed in a small 180 °C oven and baked for 5 minutes with continuous flushing to regenerate the sorbent material.

Site Characterization Penetrometer and Analysis System (SCAPS)

The SCAPS Program is a Tri-Service effort to develop sensor and hybrid sensor/sampler technologies to utilize the capabilities of cone penetrometer technology for characterizing subsurface contamination at military installations. Cone penetrometry has long been used to characterize soil for geotechnical parameters such as soil classification, strength, and liquefaction potential. This is accomplished by advancing (pushing) a standard cone penetrometer probe by hydraulic rams into the ground and measuring the resistance to penetration.

The SCAPS truck (Figure 4) is a standard 18.2 MT (20-ton) cone penetrometer platform used to advance contaminant and geotechnical sensing probes. The forward portion of the SCAPS truck houses the hydraulic rams used to translate the weight of the truck (reaction mass) into pushing force. The combination of reaction mass and hydraulics can advance a 1-meter-long by 3.57-cm diameter steel rod into the ground at a rate of approximately 1 meter per minute in accordance with American Society of Testing and Materials (ASTM) Method D3441 (ASTM 1995). The rods, various sensing probes, or sampling tools can be advanced to depths in excess of 50 m in naturally occurring soils. As the rods are withdrawn, grout can be injected through 6.2-mm- (1/4-in.-) diameter tubing within the interior of the some SCAPS probe umbilical cables, hydraulically sealing the push hole. The TDS probe is currently not configured for retraction grout. Also, while the rods are being withdrawn, they are cleaned within a hot-water manifold housed outside and beneath the truck. The rinse water is contained for proper handling and disposal.



Figure 4. Army SCAPS truck

The rear portion of the truck is comprised of a data acquisition room in which components of the SCAPS sensor technologies and onboard computers are located. An ITMS and associated laboratory equipment are installed in the data acquisition room during TDS field investigations.

The standard cone penetrometer probes are instrumented with strain gauges measuring cone resistance and sleeve friction in accordance with ASTM Standard D3441. The soil type is then determined from a ratio of cone resistance and sleeve friction using one of the empirically derived classification schemes (Lee et al. 1994; Olsen 1988). The soil class information is crucial to selecting the depth and soil strata for sample collection.

Personnel Training Requirements

Personnel operating the SCAPS CPT platform are trained in installing groundwater monitoring wells and other traditional drilling methods. Operators of the ITMS vary in skill and training, but usually have some experience in operating standard laboratory equipment. All personnel are required to operate computer software and to be familiar with the work environment around heavy equipment. All personnel conducting field investigations at potentially contaminated sites are required to complete the 40-hr Hazardous Waste Worker Training and annual 8-hr Hazardous Waste Worker Update Training. Other than health and safety training requirements, there is no mandated training required to operate the CPT technology or the ITMS.

Advantages of the Technology

The TDS is an in situ field-screening technique for characterizing the subsurface distribution of VOC contamination before installing bore holes. The method is not intended to be a complete replacement for traditional soil bores, but a means to optimize the placement of a reduced number of bores to achieve site characterization and monitoring. Using a CPT platform, the TDS system provides near real-time field screening of the distribution of VOC contamination at hazardous waste sites. The system is configured to quickly and cost-effectively distinguish VOC contaminated areas from uncontaminated areas and provide semiquantitative estimates of soil VOC contaminant concentration. This capability allows further investigation and remediation decisions to be made more efficiently and reduces the number of samples that must be submitted to laboratories for analysis. In addition, the SCAPS CPT platform allows for the characterization of contaminated sites with minimal exposure of site personnel and the community to toxic contaminants, and minimizes the volume of investigation-derived waste generated during conventional site characterization activities.

Limits of the Technology

This section discusses the limits of the SCAPS TDS system, as they are currently understood.

Truck-mounted cone penetrometer access limits

The SCAPS CPT support platform is a 18.2 MT (20-ton), all wheel drive diesel-powered truck. The truck has a minimum access width of 3 m (10 ft) and a height clearance of 4.6 m (15 ft). It is conceivable that some sites, or certain areas of sites, might not be accessible to a vehicle of this size and weight. The access limits for the SCAPS CPT vehicle are similar to those for conventional drill rigs and heavy excavation equipment.

Cone penetrometer advancement limits

The CPT sensors and sampling tools may be difficult to advance in subsurface lithologies containing cemented sands and clays, buried debris, gravel units, cobbles, boulders, and shallow bedrock. As with all intrusive site characterization methods, it is extremely important that all underground utilities and structures be located using reliable geophysical equipment operated by trained professionals before undertaking activities at a site. This should be done even if subsurface utility plans for the site are available for reference.

Thermal desorption sampler limitations

Limitations of the TDS system are in three categories: maintenance and mechanical functioning; the ability to take and expel a physical soil sample; and analyte vapor recovery from the soil sample. As with any device deployed through subsurface strata, a certain amount of wear and maintenance is to be expected. The system needs to be checked for leaks and the seals and o-rings checked daily for wear. Since the movable piston is also the tip of the TDS probe, the elevated ram force required to push through densely packed strata such as cemented sands, gravel or cobbles may cause the locking lugs to jam and prevent the TDS from opening. Also due to the small diameter of the sample port, rocks and cobbles may prevent soil from entering the sample chamber. Densely packed clays can swell after entering the sample chamber. After drying, the sample forms a hardened plug that can be difficult to eject without bringing the sampler to the surface.

The upper limit of detection for the TDS is determined by the system's ability to completely desorb analytes from the soil sample. Recovery is a function of the desorption efficiency and the completeness of the seal at the bottom of the sample chamber. The TDS design assumes that the soil material will fill the sample chamber and plug the bottom opening to form a seal. Loosely packed soils may form an incomplete seal. The completeness of the seal is determined by monitoring the gas flows down into the TDS and then back up through the manifold. Vacuum applied to the exit end of the sorbent trap is used to augment the gas flow by creating a gradient in favor of the gas returning up the analyte line and into the trap. During TDS development, soil type and moisture content were shown to affect analyte desorption efficiency with wet clays having the lowest efficiencies (Myers et al. 1995). By keeping temperatures above 170 °C during the desorption process and extending the sampling time to 20 minutes, analyte recovery can be maximized while keeping the sampling period down to a reasonable length of time.

ITMS limitations

The ITMS methodology used to identify and quantitate desorbed VOC contaminants from the TDS follows EPA SW-846 draft Method 8265. This method is intended for field screening applications using an ITMS. Because the ITMS does not utilize a separation technique, it cannot distinguish between

analytes that yield identical mass fragments. For example, 1,1-dichloroethene, cis-1,2-dichloroethene and trans-1,2-dichloroethene are identified by the same mass ion (96) and cannot be distinguished from each other. Results for this mass ion are reported as total dichloroethene (DCE). Ethylbenzene, toluene, and xylenes are also identified with the same mass ion (92) and are reported as a total. It should be noted that the current laboratory method, EPA SW-846 8260B (U.S. EPA 1995), using gas chromatography separation with mass spectrometry detection (GC/MS) is not able to differentiate some analyte pairs such as meta- and para-xylene.

A second limitation is associated with high concentrations of contaminants such as trichloroethylene (TCE) whose mass ion (132) can fragment into smaller mass ions that can cause false positive responses for total DCE and vinyl chloride. It may be necessary to raise the lower limit of detection for some analytes to reduce the probability of false positives. A third limitation associated with the ITMS instrumentation used during this demonstration was the low dynamic range of the instruments. Essentially all analytical systems have upper limits of detection as well as lower limits of detection. The upper limit of detection for the ITMS is determined by the upper limit of the number of molecules that it can analyze before the detector is "saturated" with ions. Without an automatic gain control to adjust for high concentrations of analyte introduced into the system at any point in time, the ITMS detector can become saturated causing the analytical response to flatten out as the concentration of analyte increases. To compensate for this, the ITMS operator makes a series of dilutions to bring the analytes of interest into range of the calibration curve. Contaminants with lesser concentrations could be masked or diluted out during the analysis if the analyst focuses on the contaminant with the highest concentration. This diluting out effect is not unique to ITMS analysis. However, when coupled with mass ion fragmentation and the lack of a chromatographic separation, it could have a significant impact on analyte reporting limits.

Extremely high level contamination carryover

The effective dynamic range for the TDS is determined by three factors: the dynamic range of the ITMS; the desorption efficiency from various soil types; and the potential for carryover or cross contamination between samples after desorption. Extremely high levels (greater than 10 mg/kg) of VOC contamination will cause carryover of analytes between successive samples. That is, after desorption of a very high level sample, residual VOC analytes may remain in the lower portion of the TDS analyte transfer line where they slowly desorb into successive samples over time. This is considered sample carryover between sampling events. While this residual carryover can have an additive effect on the reported concentration of a sample, it mostly impacts the lower limit of detection. This problem cannot be completely eliminated, but the effects of sample carryover can be controlled. A system blank is analyzed after every TDS sampling event. During the analysis of blank samples, carryover is present when VOC analytes are detected above system background response. When carryover is detected the sample transfer lines are purged with inert gas until the system blanks return to normal. This procedure requires approximately 30 min,

equivalent to approximately two-thirds the time required for a normal TDS sampling event. After an extremely high level sample has been analyzed, the TDS system can be removed and a backup TDS system installed to allow sampling to continue while the contaminated system is purged.

3 Demonstration Design

This section discusses the demonstration objectives, monitoring procedures, and facilities visited during the demonstration.

Performance Objectives

The primary objectives of this demonstration were to evaluate the TDS sampling technology in the following areas:

- a.* Its performance compared to conventional sampling and analytical methods.
- b.* The logistical and economic resources necessary to operate the technology.
- c.* Data quality.
- d.* The range of usefulness in which the technology can be operated.

Secondary objectives for this demonstration were to evaluate the SCAPS TDS technology for reliability, ruggedness, and ease of operation.

Physical Setup and Operation

Five sites were investigated during the field phase of this demonstration. Sites were selected in different geographic locations to facilitate exposure to soils with varying geophysical properties and to facilitate wide exposure to user communities. Sites were selected based on the following criteria:

- a.* Known soil VOC contamination in concentrations from low ng/g to µg/g.
- b.* Subsurface geology sufficiently complex to demonstrate the advantage of rapid on-site analysis compared to conventional site characterization practices.

The five demonstration sites selected and dates when visited are shown in Table 1.

Table 1 TDS System Demonstration Locations and Dates	
Facility	Demonstration Date
Bush River Study Area U.S. Army Aberdeen Proving Ground Edgewood, MD	June 1996
Davis Global Communication Site McClellan Air Force Base, Sacramento, CA	December 1996 and February 1997
U.S. Cold Regions Research and Engineering Laboratory Hanover, NH	June 1997
Lake City Army Ammunition Plant Independence, MO	June 1998
Longhorn Army Ammunition Plant Karnack, TX	August 1998

Monitoring Procedures

Soil samples were collected by traditional soil core methods from a region within 0.3 m (1 ft) laterally and ± 2.5 mm (0.1 in.) vertically of each in situ TDS system analysis location. This was accomplished by centering the length of the soil core on the TDS analysis depth. After the soil core was retrieved, the soil core was subsampled three times at a depth corresponding with the 5-cm (2-in.) in situ TDS analysis. Two of the subsamples were collected and preserved according to EPA Method 5035. These verification samples were sent to an off-site laboratory and analyzed by EPA Method 8260B.

The third subsample was taken with a stainless steel syringe designed to fit into an adapter fitted on the end of the TDS probe (Figure 5). The syringe was pre-weighed, filled with sample, then re-weighed and placed into the heated TDS sample chamber where it was desorbed and analyzed under the same conditions as the in situ TDS sample. The dried, desorbed soil plug was collected and preserved according to EPA Method 5035 procedures and sent to the off-site laboratory along with the verification samples for analysis.

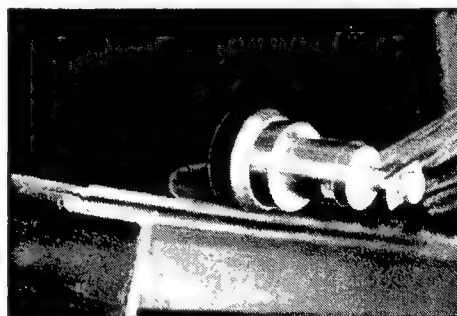


Figure 5. Ex situ TDS mode

Validation samples were analyzed using this ex situ method in order to minimize the effects of VOC heterogeneity distribution in the soil and to provide a direct comparison of sampler and laboratory validation results.

The TDS system analytical results are reported in concentrations of $\mu\text{g/g}$ in soil; the same concentration units reported by EPA Method 8260B analysis. Therefore, direct comparison of the SCAPS TDS system data with that from the verification sample analyses is simple and straightforward. The strength of

comparisons between the TDS data and the conventional laboratory method of analysis for verification samples was evaluated using least squares linear regression over the entire concentration range of data collected by each method at every site investigated. The TDS data and verification data were considered to strongly agree if the correlation coefficient of the linear regression was in the range of 0.8-1.0 and the slope of the regression line was 1.0 ± 0.3 .

Demonstration Site/Facility Background and Characteristics

The following sections provide information about each of the last three sites visited during the demonstration of the SCAPS TDS System.

Cold Regions Research and Engineering Laboratory

The U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) is located on 12.1 ha (30 acres) of land, west of and adjacent to State Highway 10, 2.4 km (1.5 miles) north of Hanover, NH.

CRREL history. The CRREL was established February 1, 1961 by the U.S. Army Corps of Engineers to combine the work of two predecessor organizations: the Snow, Ice, and Permafrost Research Establishment and the Arctic Construction and Frost Effects Laboratory. The CRREL performs basic and applied research in snow, ice and frozen ground. The CRREL also provides the U.S. Department of the Army with practical engineering research to develop equipment and procedures for applications in cold regions.

The CRREL site contains several locations where past spills, disposal practices, and operations have contaminated soils and ground water. Past investigations (Little 1994) have identified and prioritized 16 Areas of Concern (AOC) where contaminant sources may be located. Two AOCs were suitable for TDS interrogation (Figure 6).

Area of Concern 9 is located in the vicinity of the Ice Well, i.e., a cased boring fitted with a refrigeration coil for freezing water in the boring. The 0.9-m (3-ft) diameter, approximately 61-m- (200-ft-) deep Ice Well was formerly used for testing ice-drilling technologies and not constructed or used for injection or withdrawal of fluids from the ground. Trichlorethene was used in refrigeration lines and drilling fluid mixtures. This area may also contain TCE-contaminated soils as a result of a 1970 explosion in a formerly used TCE tank in AOC 1. This explosion released approximately 11 kl (3,000 gal) of TCE to the pavement and nearby unpaved area to the west of AOC 1. The refrigeration system for the Ice Well is no longer in operation, but liquids and ice still exist within this well. AOC 9 is approximately 30 m (100 ft) west of AOC 1.

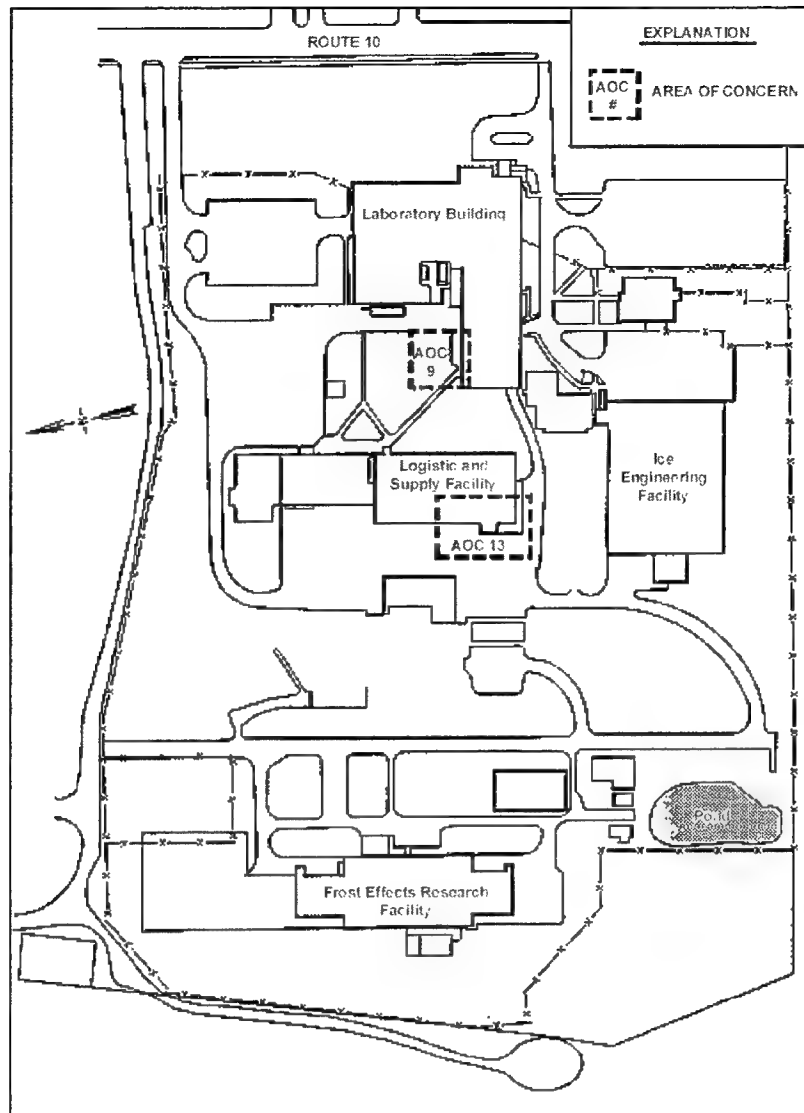


Figure 6. U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory, Hanover, NH

CRREL characteristics. The CRREL is located in the upper Connecticut River Valley on terraced unconsolidated glacial deposits. Despite modification of the topography by development, CRREL has three main terraces at elevations ranging from 158 to 140 m (520 to 460 ft) above mean sea level (msl). The eastern third of CRREL, including AOC 9, is located on the upper terrace. The upper terrace slopes gently down to the west. The middle terrace is very narrow, generally less than 30 m (100 ft), and is covered by asphalt. It contains AOC 13. The geology of CRREL consists of two main geological units: overburden sequence and bedrock. The overburden consists entirely of glaciofluvial and glaciolacustrine sediments. These soils are deep and well drained with silty and sandy textures. From east to west across the CRREL site, the soils consist primarily of Hitchcock silt loam and Windsor loamy fine sand. Silt imbedded with layers of fine sandy silt is commonly found during completion of soil

borings. The sandy silt layers can range from less than 3 cm (1 in.) to several meters. Beneath the silt is a layer of fine silty sand, which forms the basal lacustrine unit for the eastern two-thirds of CRREL. Moisture content determined from soil samples collected during the SCAPS TDS VOC sampler demonstration indicated a general trend of decreasing moisture with depth in the vadose zone. Soil moisture varied from 20 percent near the surface to 5 percent at 37 m (120 ft) below ground surface (BGS) at AOC 9. The bedrock consisted of poly-deformed metasedimentary rock. Water table depth ranges from 24 to 46 m (80 to 150 ft) BGS. The maximum depth pushed during the TDS demonstration was 18 m (60 ft) BGS.

Previous investigations between 1990 and 1996 (Little 1994; McKay 1997) identified soil and groundwater contamination at AOC 9 and 13. These investigations have included hand auger borings, drilling and sampling shallow borings, and drilling and sampling deep soil borings to bedrock. In 1996, TCE was detected in soil samples taken in AOC 9 near the Ice Well. Concentrations were highest at 5.5 m (18 ft) BGS. In 1996, the CRREL site was used to validate the SCAPS chlorinated solvent sensor. Concentrations of TCE detected at AOC 13 ranged from 0.05 mg/kg to 24 mg/kg, with the highest concentrations found at 17 m (56 ft) bgs. In addition to TCE, traces of DCE and vinyl chloride were detected during the 1996 investigation.

Lake City Army Ammunition Plant site

The Lake City Army Ammunition Plant (LCAAP) is located on approximately 1,600 ha (3,955 acres) in Jackson County, MO, mostly within the eastern corporate boundary of Independence, MO, and 37 km (23 mi) east of Kansas City, MO.

LCAAP history. The LCAAP is an U.S. Army Armament, Munitions, and Chemical Command installation which manufactures small arms ammunition. Operations at LCAAP include manufacturing, storage, test firing, waste treatment, and waste disposal.

The LCAAP consists of 33 "areas" that contain approximately 131 suspected or confirmed contaminated sites or solid waste management units (SWMUs). The TDS investigations took place in the Northeast Corner Operable Unit, Area 17.

LCAAP characteristics. The LCAAP lies within the Central Lowlands Physiographic Province near the boundary between the Osage Plains and the Dissected Till Plains. This section is characterized as a plain of low relief with gently rolling topography comprised of broad, shallow valleys and low-gradient meandering streams. The surface topography in the vicinity of LCAAP consists of rolling uplands traversed by broad stream valleys and flood plains of the Missouri River and the Little Blue River. The former flood plain averages about 3 miles in width in this area, with a surface elevation of approximately 224 m (735 ft) above sea level. Elevations on the upland surface average between 244 and 274 m (800 and 900 ft).

The north and west portions of LCAAP are flat, characteristic of an alluvial plain. The south and east portions of LCAAP are uplands created by headward erosion that exhibit moderate relief with narrow-crested ridges and 46 to 49 m (150 to 60 ft) of relief from valley floor to ridge crest. Area 17, within the Northeast Corner Operable Unit, is typical of a ridged area underlaid by uplands sedimentary rocks. Depth to bedrock at the oil and solvent pit area was approximately 12 m (40 ft).

Area 17 consists of four specific areas: the current sanitary landfill; the waste, glass, paint and solvents area; the current pistol range; and the oil and solvent pits area. The oil and solvent pits area consists of three closed disposal pits located immediately adjacent to the current sanitary landfill. Two of the three pits were used for disposal of grease and oil, waste solvents, and waste oils. The easternmost pit was used for disposal of demolition waste and domestic refuse. The western and central pits were opened in the 1960s and closed in 1979. The pits occupied an estimated surface area of 0.23 ha (25,000 sq ft) and reportedly received approximately 283 cu m (10,000 cu ft) of waste. The easternmost pit was opened in 1977 and closed in 1979. Fill thickness of up to 3 m (10 ft) was indicated by a soil boring drilled during the 1990 remedial investigation work. Closure of the three pits did not involve the use of an engineered cover system. Currently, the pits are heavily vegetated with a soil cover typically less than 0.3 m (1 ft) thick. Stressed vegetation and small barren areas at the ground surface have been noted at this site. The TDS demonstration took place at the oil and solvent pits area along the gravel road running beside the central pit (Figure 7).

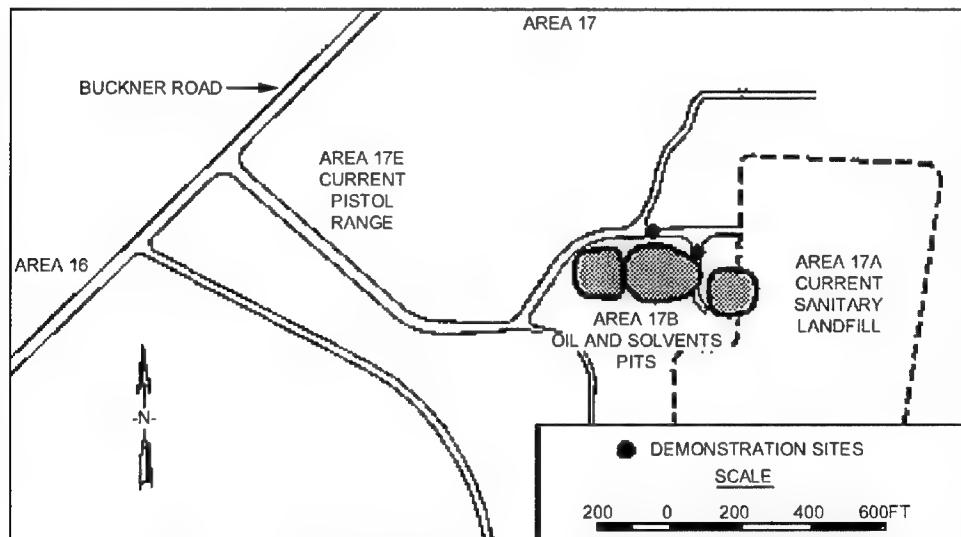


Figure 7. Lake City Army Ammunition Plant, Independence, MO

Longhorn Army Ammunition Plant site

The Longhorn Army Ammunition Plant (LHAAP) is located on 3,450 ha (8,523) acres in the northeast corner of Harrison County near Karnack, TX, approximately 23 km (14 miles) northeast of Marshall, Texas, and approximately

64 km (40 miles) west of Shreveport, LA. The LHAAP is a government-owned, contractor-operated industrial facility operated under the jurisdiction of the U.S. Army Industrial Operations Command.

LHAAP history. Operations at the LHAAP began in 1942 for the production of TNT flake by Monsanto Chemical Company and continued through August 1945. From 1952 until 1956, Universal Match Corporation produced pyrotechnic ammunition such as photoflash bombs, simulators, hand signals, and 40-mm tracers. In 1955, Thiokol Corporation began operation of the Plant 3 area rocket motor facility. In 1965, production of pyrotechnic and illuminating ammunition was re-established. These operations consisted of compounding pyrotechnic and propellant mixtures, load, assemble, and pack (LAP) activities that accommodated receipt and shipment of containerized cargo. The LHAAP also maintained standby facilities and equipment for mobilization planning. The installation has also been responsible for the static firing and elimination of Pershing I and II rocket motors in compliance with the Intermediate Range Nuclear Force Treaty between the United States and the former Union of Soviet Socialist Republics. Currently the LHAAP has no permanent operating contractor. The plant is now closed and is scheduled to be returned to state and/or private ownership.

The LHAAP was placed on the national priority list in 1990. Fifty sites are included in the restoration effort: 4 open burning areas; 13 industrial areas; 5 burial pits; 5 sumps/tanks; 4 treatment plants; 16 storage areas; and 3 landfills. The current status of the areas ranges from site investigation to interim remedial action. Contaminants consist of explosives and VOCs in soil, groundwater, and surface water.

LHAAP characteristics. The LHAAP site is characterized by mixed pine-hardwood forests that cover gently rolling to hilly terrain with an average slope of 3 percent towards the northeast. Most of the terrain at LHAAP slopes 3 percent or less, but slopes as steep as 12 percent are common in the western and northwestern portion of the installation and also along the Harrison Bayou flood plain. Caddo Lake and Goose Prairie Bayou form the northeastern border. Ground surface elevations on LHAAP vary from 52 to 102 m (170 to 335 ft) above sea level. All surface water from LHAAP drains northeastward into Caddo Lake via four drainage systems: Saunder's Branch, Harrison Bayou, Central Creek, and Goose Prairie Creek.

The LHAAP is situated on an outcrop of the Wilcox Group, which crops out over a large part of the eastern half of Harrison County. The Wilcox Group lies beneath more than 99 percent of the LHAAP site and consists of interbedded sandstones, siltstones, and shales that are variously light gray, red, brown and/or tan. Regionally, the Wilcox Group has a maximum thickness of 213 m (700 ft).

Surficial soils consist of medium sandy clays exhibiting plasticity with some zones of higher plasticity clays to a depth of 1.2 to 3 m (4 to 10 ft) BGS. Beneath this surficial layer, the soils typically consist of low plasticity clays and silty and clayey-sands to a depth of at least 18 m (59 ft) BGS. These deposits are typical of the Wilcox Group. Alluvial deposits also occur at LHAAP along the

drainage systems featured across the facility. Typical deposits include interbedded fine-grained clays, silts, and sands.

Groundwater generally occurs under unconfined conditions, whether in the alluvial or Wilcox Group deposits. Perched and local confining conditions frequently occur within the Wilcox Group deposits due to the high clay content and highly variable stratigraphy. The base of the Wilcox Group water-bearing zone beneath LHAAP is defined by contact of the Wilcox Group with the underlying Midway Group. The Midway Group consists predominantly of low permeability clay that yields little or no water. The Wilcox Group is considered as the base of fresh water in the area. The depth to groundwater across the facility ranges from 0.3 to 21 m (1 to 70 ft) BGS, with depth to groundwater typically being 3.6 to 5 m (12 to 16 ft). The regional groundwater flow direction beneath the facility is generally towards Caddo Lake but varies by site location. At the TDS demonstration location site, ground water was found in thin seams of sand and gravel above zones of clay.

The TDS demonstration took place in the Plant 3 area rocket motor facility sumps project area (Figure 8). The sumps project area consists of 125 underground sumps and 20 waste rack sumps located throughout the LHAAP production area. Manufacturing areas at LHAAP were washed down with water to reduce propellant, explosive, and pyrotechnic (PEP) dusts which would otherwise collect and pose a safety hazard. Water deactivates ignition-sensitive compositions. To dissolve difficult chemical binders, chlorinated solvents were also utilized in the clean manufacturing areas. These solvents and PEP compositions were washed into sumps with large volumes of water. Based upon previous investigations (Target Environmental Services 1994; USACE Tulsa 1996), VOC contaminants in the groundwater include TCE (0.010 to 5.0 mg/L), total DCE (0.020 to 2.0 mg/L) and, tetrachloroethane (around 0.050 mg/L).

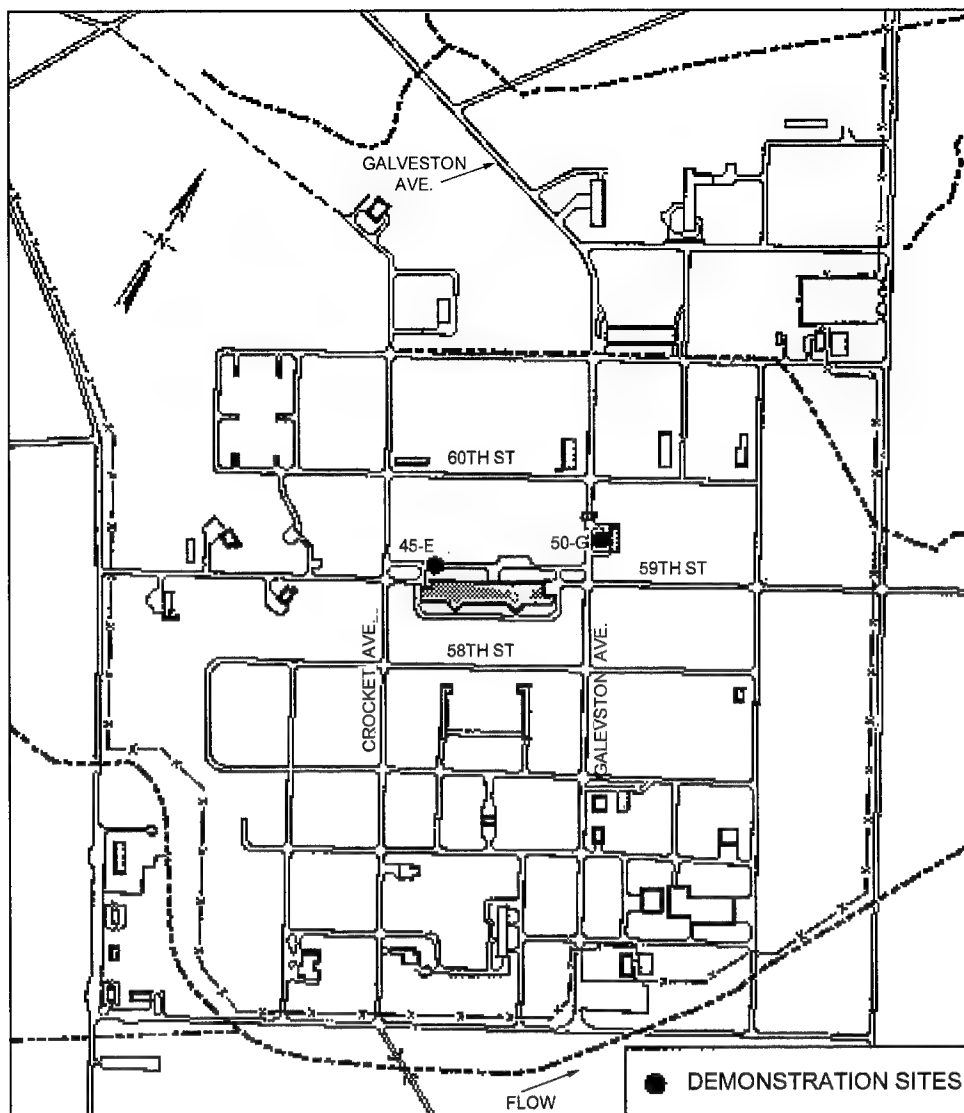


Figure 8. Longhorn Army Ammunition Plant, Marshall, TX

4 Performance Assessment

This section provides the results for each demonstration along with an evaluation of the TDS system with respect to each of the performance objectives listed in Chapter 3.

Comparison of TDS Sampler Technology with Conventional Technology

The TDS production at each of the five demonstration sites is shown in Table 2.

Table 2 Summary of Field Sampling at TDS Demonstrations Sites							
Site Name	Stratigraphy Penetrations	TDS Penetrations	TDS in situ Samples	TDS ex situ Samples	Verification Samples	TDS Maximum Depth m (ft)	TDS Total Depth, m (ft)
BRSA	18	18	64	NA	68	10.4 (34)	8.7 (278)
DGCS	5	11	28	24	39	15.8 (52)	122 (400)
CRREL	4	8	37	37	254	18.3 (60)	111 (365)
LCAAP	3	5	16	16	98	4.0 (13)	15.8 (52)
LHAAP	5	8	26	26	173	5.5 (18)	37.5 (123)

The TDS system was designed to provide near real-time screening of VOC contamination at hazardous waste sites. During the five ESTCP demonstrations, the TDS system was used to detect chlorinated solvent and BTEX contamination at depths up to 18.3 m (60 ft) BGS in a wide range of soil types and soil moisture conditions. There were 171 in situ TDS samples analyzed in 50 separate TDS penetrations. More than 600 verification samples were collected for conventional analysis by Method 8260B to evaluate the TDS results. Graphics of the comparisons made for these data are given in Figures 9 through 12.

Results from the first two demonstrations at the Bush River Study Area (BRSA) and the Davis Global Communications Site (DGCS) revealed flaws in both the validation sample collection and TDS system operation procedures. Subsequent demonstrations were completed with re-evaluated TDS system operation and verification test procedures. For this reason, the data obtained

from the BRSA and the DGCS should not be considered representative of the TDS system's true capabilities.

As stated in Chapter 3, if the correlation coefficient of the linear regression (r^2) is in the range of 0.8 to 1.0 and the slope of the regression line is 1.0 ± 0.3 , the data is said to strongly agree. Based upon the combined statistical comparisons for LCAAP and LHAAP, these data sets can be said to strongly agree. The CRREL data set, even with its varied concentrations, had a correlation coefficient of 0.7 and a regression slope of 1.0. Identification of vinyl chloride soil gas at levels greater than $1 \mu\text{g/g}$ is a significant accomplishment. Because there were so few samples containing BTEX, the TDS was not adequately tested for those compounds.

Closer inspection of the analytical results shows that the predominating VOC at each demonstration had the strongest agreement between TDS system results and validation results. At CRREL the primary VOC contaminant was TCE ($r^2 = 0.7$, slope = 1.0) the secondary contaminant was DCE ($r^2 = 0.2$, slope = 1.6). At LCAAP, total DCE ($r^2 = 0.8$, slope = 0.8) and vinyl chloride ($r^2 = 0.5$, slope = 1.1) were the major contaminants. At LHAAP, TCE was the primary VOC ($r^2 = 1.0$, slope = 1.1) and total DCE ($r^2 = 0.6$, slope = 0.5) was secondary. In each case the predominant contaminant had a higher mass quantitation ion than the secondary contaminant (i.e., TCE 132 m/z, DCE 96 m/z, vinyl chloride 62 m/z). The difficulties analyzing total DCE in the presence of TCE are primarily due to the lack of chromatographic separation. Without separation the contaminants reach the ion trap at the same time. The ion trap breaks the higher mass compound into fragments. These smaller fragments can contribute to the signature of the lower mass compounds thereby potentially creating false positives. This phenomenon was experienced at LHAAP.

Cold Regions Research and Engineering Laboratory

Soil samples were collected from the vadose zone at CRREL.

Figure 9 shows a comparison between the analysis results of the TDS system in the ex situ model and the validation analysis results. There were no false positives or false negatives. The poor total DCE correlation is possibly the result of the extreme heterogeneity of the VOC distribution discovered through high-density verification sample collection (Figure 10).

Excessive push rod side wall friction prevented the TDS probe from advancing deeper than 18.3 m (60 ft) BGS. These types of limitations are not unique to the TDS system. In instances when the sample chamber did not seem to fill with soil, the sampler was closed and pushed another 0.2 to 0.3 m (6 to 12 in.) and the sampling process continued.

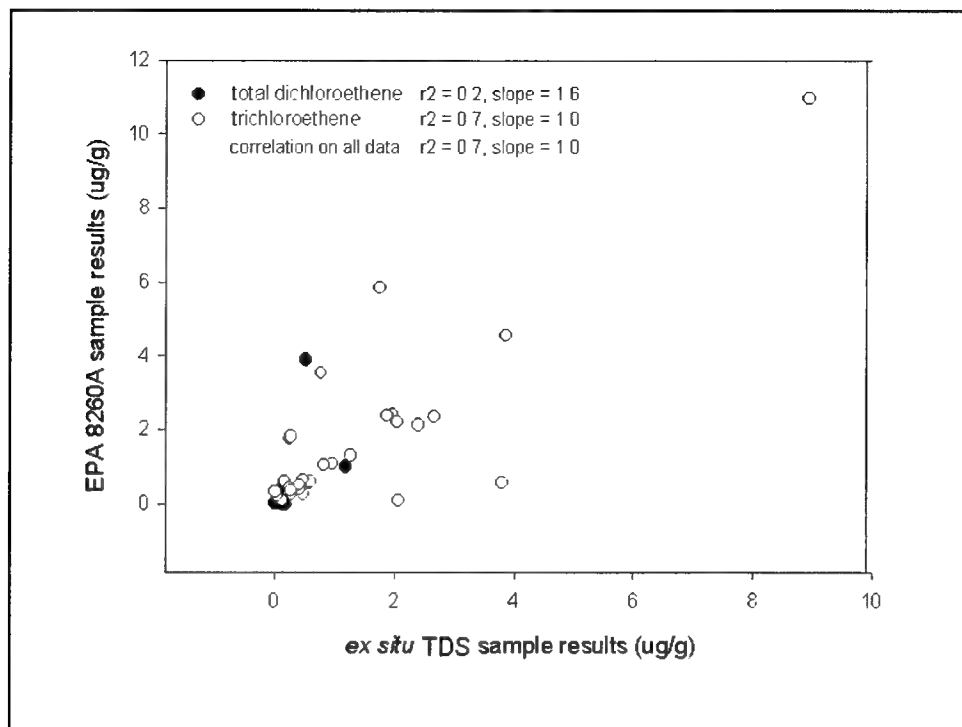


Figure 9. CRREL data comparison

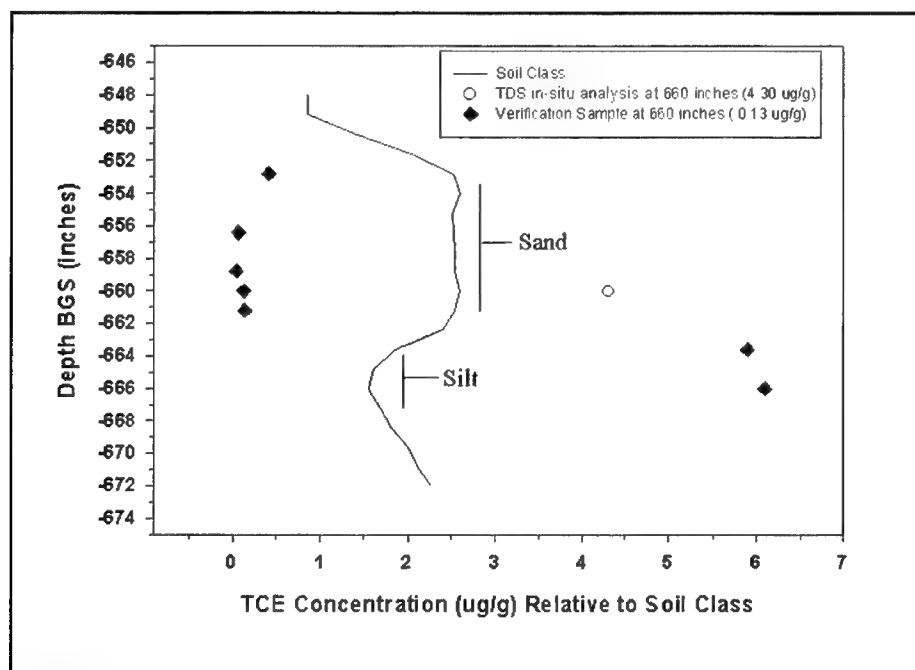


Figure 10. Changes in TCE concentrations at CRREL relative to soil type and depth. Soil class changes from sand to silt between 664 and 670 in. BGS

Lake City Army Ammunition Plant

In situ analysis was performed in the vadose zone adjacent to an oil and solvent pit. VOC gases were the most probable source of contamination.

Figure 11 shows a comparison between the analysis results of the TDS system in the ex situ mode and the validation analysis results.

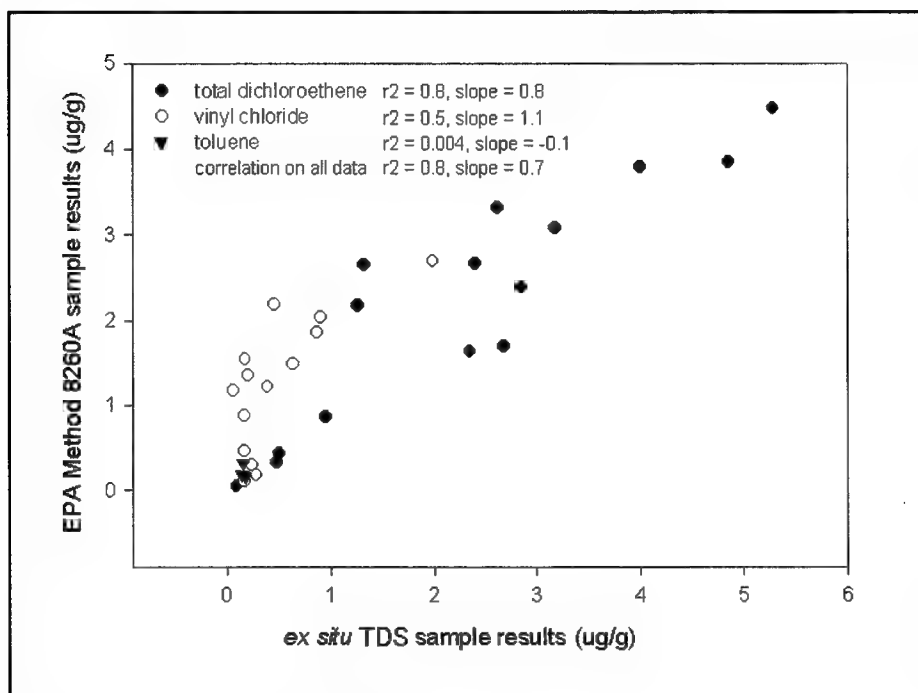


Figure 11. LCAAP data comparison

The TDS system detected total DCE in 12 of the 16 samples and no false positives or false negatives were found based on a comparison with the validation analysis results. Toluene was detected in three in situ TDS analysis from a single penetration and was confirmed in both the ex situ TDS and validation sample analysis. Tetrachloroethene (PCE) was detected in verification samples from four of the penetrations, but was not detected by the TDS system in either the in situ or the ex situ analysis modes.

Longhorn Army Ammunition Plant

In situ analysis was performed in the saturated and unsaturated bedded layers of silty sands and clay. Volatile organic compounds found at LHAAP included TCE and total DCE. Figure 12 shows a comparison between the analysis results of the TDS system in the ex situ mode and the validation analysis results. The analysis of verification samples revealed a false positive for total DCE. However, the high concentration of TCE was isolated as the cause of the total DCE response.

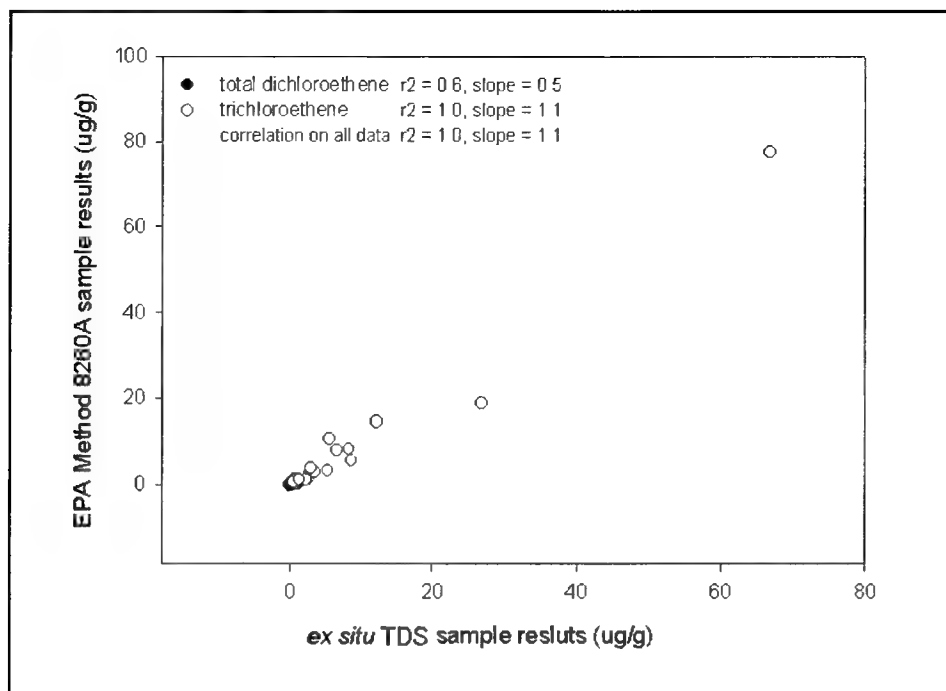


Figure 12. LHAAP data comparison

Sample Matrix Effects on the TDS System

The TDS system was deployed successfully in five geographic locations, in a variety of soil types ranging from sands to silts and clays. However, it was found that clay soil and soils with high moisture content impeded desorption of the contaminant from the in situ sample. This impediment was quantified by completing an in situ analysis of a soil sample by the TDS system. After the in situ analysis was complete, the TDS probe was then brought to the surface, the desorbed soil sample was ejected from the TDS probe, and collected in methanol for laboratory analysis. The analysis results are presented in Table 3.

Table 3			
Desorption Efficiencies by Matrix and Contaminant			
Soil Type		DVTD10-52	CRTD01-40-2
		Clay	Silt
Moisture Content (%)		21	24
TCE (ug/g)	in situ	0.079	31.4
	offsite laboratory	0.029	0.003
	desorption efficiency	73.1%	99.9%
PCE (ug/g)	in situ	0.283	NA
	offsite laboratory	0.150	NA
	desorption efficiency	65.4%	
DCE (ug/g)	in situ	NA	1.16
	offsite laboratory	NA	0.341
	desorption efficiency		77.3%

Since this sample was collected in situ and subjected to extreme temperature, it should not contain VOCs. The fact that the soil samples from the clay soil have some residual VOCs indicates a less than ideal desorption efficiency. The largest difference is noted in the TCE analysis results, the clay sample having significantly less recovery, particularly given the large difference in initial concentrations (0.079 $\mu\text{g/g}$ for clay versus 31.4 $\mu\text{g/g}$ for silt).

These field data support laboratory studies that were done to evaluate the effects of soil moisture content on VOC desorption efficiencies (Myers et al. 1995). These controlled studies resulted in the same conclusion that clay soils and saturated soils had the lowest desorption efficiencies.

To improve analyte recovery and compensate for the reduced desorption efficiencies, temperatures and desorption times were increased as the demonstration progressed.

Soil type can also affect the mechanical functioning of the TDS probe. Gritty residue from sands can prevent the TDS probe actuator rod from closing, increase the wear and tear on o-rings, and increase the frequency of system maintenance. Densely packed clays can swell after entering the sample chamber, drying into a hardened plug that can be difficult to eject. During the course of the five demonstrations 20 percent of the 175 TDS samples either failed to eject below ground or the TDS failed to close. Most of these samples were taken in densely packed clays or coarse sand. A resizing of the stainless steel sleeve surrounding the sample chamber is expected for most of these occurrences.

Contaminant Carryover

In general, purging the TDS system for 5 to 10 minutes after sample ejection eliminated carryover. This was confirmed by analyzing the purge gas. However, during the CRREL demonstration, a TDS in situ analysis was performed to evaluate the effects of a highly contaminated sample. Concentrations in the sample selected were measured at 406 $\mu\text{g/g}$ of TCE and 30.5 $\mu\text{g/g}$ of total DCE. Figure 13 is a graphic representation of the system recovery rates that can be expected. After purging the TDS system for 50 minutes, residual concentrations inside the system were 0.90 $\mu\text{g/g}$ for TCE and 0.06 $\mu\text{g/g}$ for total DCE. While this represents a 99.8 percent decrease in contaminant carry-over, the TDS sampler would have to be purged overnight or removed from service and cleaned to achieve the 0.05 $\mu\text{g/g}$ detection limit typically used. However, these carry-over contaminant concentrations would not prohibit using the TDS system for screening purposes at sites with high levels of VOC contamination.

Quality Assurance Assessment

Each analysis, whether performed on-site by the TDS system or off-site in an analytical laboratory, is checked by the analysis of quality control (QC) check samples.

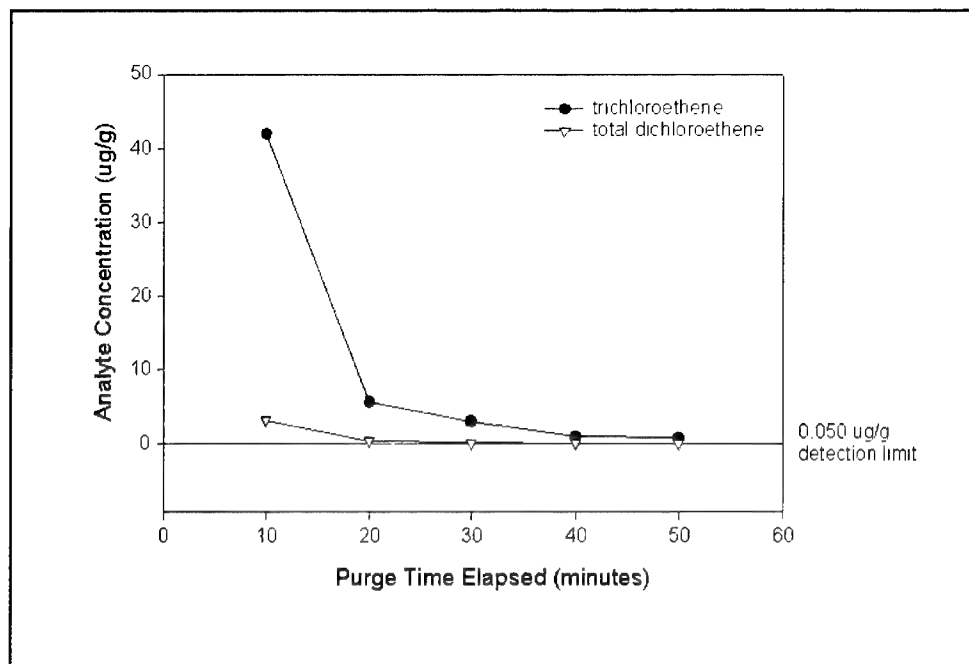


Figure 13. TDS system recovery after analysis of a highly contaminated sample

TDS system

Quality control check samples used on site for the TDS system include:

- Initial calibration standards to generate the calibration curve for each target VOC.
- Calibration checks at midday and at the end of the day.
- Performance evaluation (PE) spikes for the target VOCs each morning.
- System blanks analyzed each morning and following each TDS system analysis.

Correlation coefficients for the TDS system daily calibration curves used to quantitate the TDS analysis results were 0.97 or better. If the midday calibration check fell above 20 percent, the calibration was repeated before sample analysis resumed. Samples with VOC concentrations outside the range of the standard curve were diluted and reanalyzed. Method blanks were within acceptable limits and PE spikes for the target VOCs fell within a range of 70 to 130 percent. Based on the QC checks and the quality of the data produced, the TDS system was judged to be acceptable for continued field analysis.

The results of system blank analysis between each TDS analysis event were significantly less than the reporting limit. Time constraints did not allow field operators to wait to ensure every blank was clean before proceeding to the next

sample depth. However, if the calculated VOC concentration was less than 10 µg/g in the previous sample, the system was assumed to be clean.

Recovery from daily QC spikes was found to be dependent upon the ambient temperature during the field demonstration and upon the vapor pressure of the target VOC. The spikes were made daily in a gasbag from pure VOC standards. Recoveries exceeding 30 percent for DCE were rare at LCAAP and LHAAP where morning temperatures were near 27 °C . However, the average recoveries at LCAAP and LHAAP were 57 and 65 percent, respectively. Spike recoveries averaged 80 percent at CRREL where morning temperatures were near 18 °C. Initial TDS performance was verified in laboratory studies using spike recoveries (Myers et al. 1995). Hence, it is unlikely that the field-prepared daily spike recoveries reflect actual TDS performance. The performance of the TDS system can be controlled more accurately by adequate system maintenance, daily leak checks, and monitoring gas flow rates during sampling.

EPA Method 8260B

Quality Control check samples associated with the EPA Method 8260B verification samples include:

- a. Initial calibration standards to generate the calibration curve for each target VOC.
- b. Daily checks of the ITMS calibration.
- c. Method blanks, method spikes, method duplicates
- d. PE checks, and surrogate spikes.

In addition, 5 percent of the verification samples sent offsite were split and sent to a second laboratory for confirmation analysis. Field duplicates were taken, but due to soil and VOC heterogeneity, they could not always be considered true duplicates. Trip blanks were sent with each shipment of samples for off site laboratory analysis.

Quality Control sample analysis results associated with EPA Method 8260B were within laboratory prescribed limits. The GC/MS separates three VOCs that share the same mass quantitation ion: 1,1-DCE; cis-DCE; and trans-DCE. Results from EPA Method 8260B for these three VOCs were summed into a total DCE value for comparison to the TDS system results.

TDS Method Detection Limits

Detection limits for the TDS system were established in the laboratory prior to the demonstration. Method detection limits (MDL) were determined according to 40 CFR Part 136. Reporting limits are approximately 0.025 to 0.050 µg/g, depending on the number and concentrations of VOCs in the sample.

When a TDS sample analysis identified two or more VOCs at concentrations greater than an order of magnitude apart, the sample was diluted and reanalyzed to bring the major contaminant into calibration range. This meant that the VOC of lesser concentration was diluted out of analysis detection range. Loss of analytical information due to elevated detection limits is not unique to the TDS system. This was a continuing problem with the offsite laboratory analysis as well. For comparison purposes, analytical results with elevated detection limits were considered to be inconclusive and were omitted from the statistical comparison.

5 Cost Assessment

Determining cost performance for site characterization technologies is difficult, primarily because the point at which characterization is complete is not easily defined. The general approach is to compare relative cost on a per sample basis (for example see the Federal remedial round table's Field Sampling and Analysis Technologies Matrix at www.frtr.gov). However, this per sample comparison often means that characterization techniques, which complete analysis onsite are more expensive because of the economy of scale enjoyed by offsite laboratories. Time is the commodity saved by using in situ or onsite characterization tools. If properly used, not only are sample analysis results immediately available, but decisions that allow complete site characterization in one field deployment can be made.

TDS Sampler Cost Performance

The costs associated with TDS system operation include equipment costs for the SCAPS vehicle, expendable supplies, crew travel expenses, and labor. The cost for SCAPS field operations are well documented from previous work performed by the ERDC SCAPS and from work performed over the past four years by the three USACE District SCAPS vehicles. The average cost of operating a SCAPS truck and four-person crew in the field during production work, regardless of sensor type, is approximately \$4,500 per day.

The cost per TDS analysis (unit cost) depends on the number of TDS samples taken in a single day. The number of samples achievable in a single day depends upon several factors. The major factor is the depth of penetration and frequency of sampling along the decent as prescribed in the sampling plan. Secondly, normal CPT limitations such as on-site mobility and subsurface geology impact the amount of work achieved in one day. The majority of the time associated with a TDS unit operation is the time required to push the TDS to sampling depth, desorb the sample, purge the system (approximately 40 minutes per sample during the demonstration), and retract the push pipe after the TDS analysis is complete. The deeper the penetration depth required at a particular site, the lower the production rate and the higher the unit cost. However, it should be noted the same unit cost relationship exists for conventional drilling and soil sampling techniques. The TDS also has the capability to conduct multiple in situ sample analyses at discrete depths during a single penetration event.

Production rates obtained during this demonstration were lower than rates expected during actual production work, due in part, to the 100 percent verification of each TDS analysis location. The time required for verification sampling approximately doubled the time required at each TDS analysis location.

Cost Comparison of the TDS System to Conventional and Other Technologies

Costs associated with conventional drill rig/soil sampling are site dependent. The costs for conventional technologies were obtained from managers at each demonstration site. These costs were not always broken out in ways that could be directly comparable to the TDS sampling technology. For comparison purposes, costs associated with three technologies (SCAPS TDS onsite analysis, conventional drilling with offsite analysis, and direct push with offsite analysis) were itemized for a similar site characterization project consisting of ten 30-ft pushes and the analysis of 60 samples for VOCs. A comparison of each technology is summarized in Table 4.

When compared on a unit cost basis, the SCAPS TDS system costs fall midway between direct push technologies with offsite analysis and conventional drilling with offsite analysis. The TDS system does have the advantage of near real-time turnaround, however. During several demonstrations, immediate sample turnaround enabled the SCAPS crew to take additional samples to fill in gaps in the data set. Using conventional technology, the drill rig and sampling crew would have had to be re-mobilized. This alone is a great cost savings that cannot be factored into costs on a per unit basis.

Table 4
Comparison of Unit Costs for the TDS Sampler and Conventional Technologies

SCAPS TDS In Situ Measurement		Conventional Drilling (hollow stem auger, split spoon, and offsite analysis)		Direct Push and Offsite Analysis	
10 Pushes to 30 ft	Cost	10 Borings to 30 ft (60 soil samples for TPH analysis)	Cost	10 Borings to 30 ft (60 soil samples for TPH analysis)	Cost
6 Field Days @ \$4,500/day	\$27,000	Drilling for 300 ft @ \$50/ft	\$15,000	Drilling for 300 ft @ \$10/ft	\$3,000
Analysis for 60 samples	Included in Cost	TVOC Analysis for 60 samples @ \$200/sample	\$12,000	TVOC Analysis for 60 samples @ \$200/sample	\$12,000
Geotechnical Data for 1 sample/in.	Included in Cost	Geotechnical Analysis for 5 samples @ \$100/sample	\$500	Geotechnical Analysis for 5 samples @ \$100/sample	\$500
1 Waste Drum @ \$40/drum	\$40	28 Waste Drums @ \$40/drum	\$1,120	1 Waste Drum @ \$40/drum	\$40
Decon Water Testing	\$1,000	Decon Water Testing	\$1,000	Decon Water Testing	\$1,000
Waste Soil Testing	\$0	Waste Soil Testing	\$3,000	Waste Soil Testing	\$0
Waste Soil Disposal	\$0 (none produced)	Waste Soil Disposal for 20 Drums @ \$100/drum	\$2,000	Waste Soil Disposal	\$0 (none produced)
Decon Water Disposal for 1 Drums @ \$100/drum	\$100	Decon Water Disposal for 8 Drums @ \$100/drum	\$800	Decon Water Disposal for 1 Drum @ \$100/drum	\$100
		Geologist for 40 hr @ \$60/hr	\$2,400		
4 Man Crew	Included in Cost	Technician for 40 hr @ \$40/hr	\$1,600	Geologist for 24 hr @ \$60/hr	\$1,440
TOTAL		TOTAL		TOTAL	
Per Sample Cost for 60 Samples	\$28,140	Per Sample Cost for 60 Samples	\$39,420	Per Sample Cost for 60 Samples	\$18,080
Note: To obtain meters, multiply feet by 0.3048.					

6 Implementation Issues

Based on the results of the last three TDS technology demonstrations, the TDS system has been transitioned for onsite screening. In 1998, the technology was made available to the USACE Districts operating SCAPS vehicles. Two TDS probes are available to Tri-Service and U.S. government agency use.

While there has been limited use of TDS technology by the user community for onsite screening, the TDS technology's ability to take discrete snapshots of vadose zone VOC contamination may be an advantage for use at sites utilizing monitored natural attenuation (MNA) for remediation. Under the right scenario, this technology could be used to provide cost-effective, less-intrusive analytical snapshots of subsurface VOC natural attenuation.

Regulatory Issues

One of the objectives of this demonstration was to gather data of a quality to be used in pursuing regulatory acceptance of the TDS system at State and Federal levels. Previous experience in the Tri-Service SCAPS Program with regulatory acceptance of the Laser induced Fluorescence (LIF) sensor demonstrated that there is no clear path to regulatory acceptance of innovative environmental technologies (Lieberman 1996). Therefore, a multi-pathed approach to State and Federal regulatory acceptance was initiated early in the demonstration.

In cooperation with Dr. Marc Wise, U.S. Department of Energy Oak Ridge National Laboratory, and Dr. William M. Davis, U.S. Army Engineer Research and Development Center, ERDC, the TDS system was included with other sample inlet devices in a draft DSITMS method (Wise et al. 1997) submitted to U.S. EPA Office of Solid and Hazardous Waste (OSHW). The OSHW designated this document Draft Method 8265. It is currently under review for inclusion in the next revision of "Test Methods for Evaluating Solid and Hazardous Waste, SW 846" (U.S. EPA 1995). Drs. Wise and Davis defended the method before the Organic Methods Working Group at the annual methods review meeting in July 1997.

The TDS system is under review by the California Environmental Protection Agency, Department of Toxic Substance Control (Cal EPA-DTSC) under the state Hazardous Waste Environmental Technology Certification Program. The evaluation process includes high-level data validation of both the TDS data sets

and laboratory validation data sets. In addition, representatives of the Cal EPA-DTSC reviewed the DGCS Demonstration Plan and provided comments before the demonstration took place. Cal EPA-DTSC personnel observed the field operation of the TDS system at the DGCS and at LHAAP. The agreement for evaluation was initiated in 1998 and TDS data sets are currently under review by that office.

Lessons Learned

The most significant lessons learned in these demonstrations relate to an increased understanding of subsurface heterogeneity and its relationship to VOC distribution within the vadose and capillary zones and the complexity of attempting to statistically validate a technology associated with so many variables. The SCAPS TDS system, along with the more traditional technology utilized for validation, is only capable of taking a snapshot of the subsurface at localized points. Attempts to establish linear correlation between two samples taken 12 in. apart horizontally is not always possible. Researchers should collect as much data as possible at each demonstration site to obtain a good subsurface profile of both the geology and the extent of contamination. Sufficient verification data, collected from multiple sites, must be obtained before true statistical patterns can be recognized.

References

- American Society for Testing and Materials (ASTM). (1995). "Standard test method for deep, quasi-static, cone and friction-cone penetration tests of soil." ASTM 04.08 (D-3441), West Conshohocken, PA.
- Arthur D. Little, Inc. (1994). "Phase II remedial investigation for Cold Regions Research and Engineering Laboratory (CRREL), Hanover, NH," Volume I of III. U.S. Army Environmental Center, Aberdeen, MD.
- Lee, L. T., Davis, W. M., Goodson, R. A., Powell, J. F., and Register, B. A. (1994). "Site characterization and analysis penetrometer system (SCAPS) field investigation at the Sierra Army Depot, California," Technical Report GL-94-4, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Lieberman, Stephen. (1996). "Site characterization and analysis penetrometer system (SCAPS) validation technology demonstration report." Environmental Security Technology Certification Program (ESTCP) Final Report, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- McKay, D. (1997). "Innovative technology demonstration at the U.S. Army Cold Regions Research and Engineering Laboratory," Volume 1 of 2: Decision document, prepared for U.S. Army Environmental Center, Aberdeen Proving Ground, MD.
- Myers, K. F., Brannon, J. M., Karn, R. A., Price, C. B., Eng, D. Y., Strong, A. B., and Cooper, S. S. (1995). "Laboratory evaluation of a volatile organic compound analysis system for the site characterization and analysis penetrometer system," Technical Report IRRP-95-3, U. S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Olsen, R. (1988). "Using the CPT for dynamic site response characterization." *Specialty Conference II on Earthquake Engineering and Soil Dynamics*. American Society of Civil Engineers, Park City, UT.
- Target Environmental Services, Inc. (1994). "Soil gas survey; Longhorn Army Ammunition Plant; LHAAP-12 and LHAAP-16 (Active and old landfills), Karnack, TX", prepared for U.S. Army Engineer District, Tulsa, U.S. Army Engineer District, Tulsa, (1996). "Group IV Pre-Phase III groundwater investigation report - Longhorn Army Ammunition Plant," Tulsa, OK.

- U.S. Army Engineer District, Tulsa. (1996). "Longhorn Army Ammunition Plant, Karnack, Texas, Group IV Pre-Phase III groundwater investigation report," Tulsa, OK.
- U.S. Environmental Protection Agency. (1995). "Test methods for evaluating solid waste; Physical/chemical methods, SW-846 Third Edition," Washington, DC.
- Wise, M. B., Guerin, R. M., Thompson, C. V., and Davis, W. M. (1997). "Direct sampling ion trap mass spectrometry for the measurement of volatile organic compounds in water, soil and air," Draft EPA SW-846, Method 8265.

Appendix A

Points of Contact

Mr. John H. Ballard, ERDC SCAPS Assistant Program Manager
CERD-EP-S
Vicksburg, MS 39180
Phone: (601) 634-2446
Fax: (601) 364-2854
E-mail: ballarj1@wes.army.mil

Ms. Karen F. Myers, ERDC Project Manager
CERD-EE-C
Vicksburg, MS 39180
Phone: (601) 634-3652
Fax: (601) 634-2742
E-mail: myersk@wes.army.mil

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) February 2001		2. REPORT TYPE Final Report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Cost and Performance Report for Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) Thermal Desorption Sampler for Volatile Organic Compounds				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Karen F. Myers, Jed Costanza, Dan Y. Eng, Richard A. Karn, Karl F. Konecny, William M. Davis				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Engineer Research and Development Center 3909 Halls Ferry Road Vicksburg, MS 39180-6199				8. PERFORMING ORGANIZATION REPORT NUMBER ERDC/EL TR-01-6	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Environmental Security Technology Certification Program U.S. Army Engineer Research and Development Center 3909 Halls Ferry Road Vicksburg, MS 39180-6199				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <p>The thermal desorption sampler (TDS), developed for the Site Characterization and Analysis Penetrometer System (SCAPS) program provides in situ analysis of volatile organic compounds (VOCs) in vadose zone and saturated soils. In operation, the TDS captures an estimated quantity of soil below ground, thermally desorbs the VOCs, and transfers them to the surface where they are analyzed on a field portable ion trap mass spectrometer (ITMS). This analysis is sensitive to the low ppb range for chlorinated solvents and BETX compounds.</p> <p>The TDS was field tested at five geologically distinct sites across the country. Field data were compared to laboratory data (US EPA SW-846 Method 8260B) for validation of the technique. Data analysis indicated that the in situ analysis of the primary VOC contaminant at each site demonstrated good correlation with the validation method with a liner regression correlation coefficient between 0.8 and 1.0 and the slope of the regression line between 0.7 and 1.3. Secondary VOC contaminants of lesser concentration, demonstrated poorer correlation that could be attributed to the lack of chromatographic separation prior to the ITMS analysis.</p> <p>Cost of operating the TDS system was compared to conventional sample collection and analysis techniques. The main savings produced by using this system were a reduction in time spent characterizing a site, the reduced exposure of workers to contaminants, and the minimization of investigation wastes.</p>					
15. SUBJECT TERMS Cost and performance Ion trap mass spectrometer Site characterization TDS In situ analysis SCAPS Thermal desorption Volatile organic compounds					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 44	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UNCLASSIFIED	b. ABSTRACT	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (include area code)